Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Suppression of Voltage-Decay in Li_2MnO_3 Cathode via Re-construction of Layered-Spinel Coexist Phases

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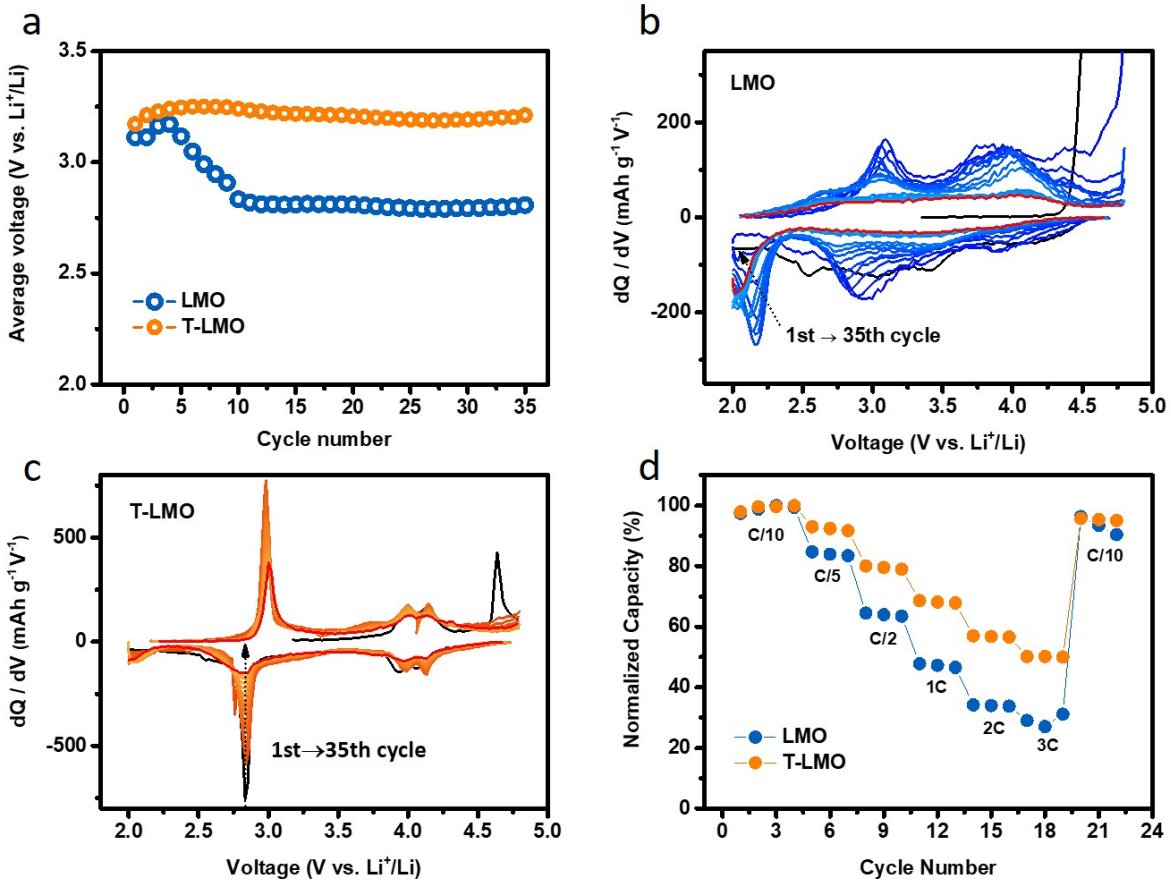
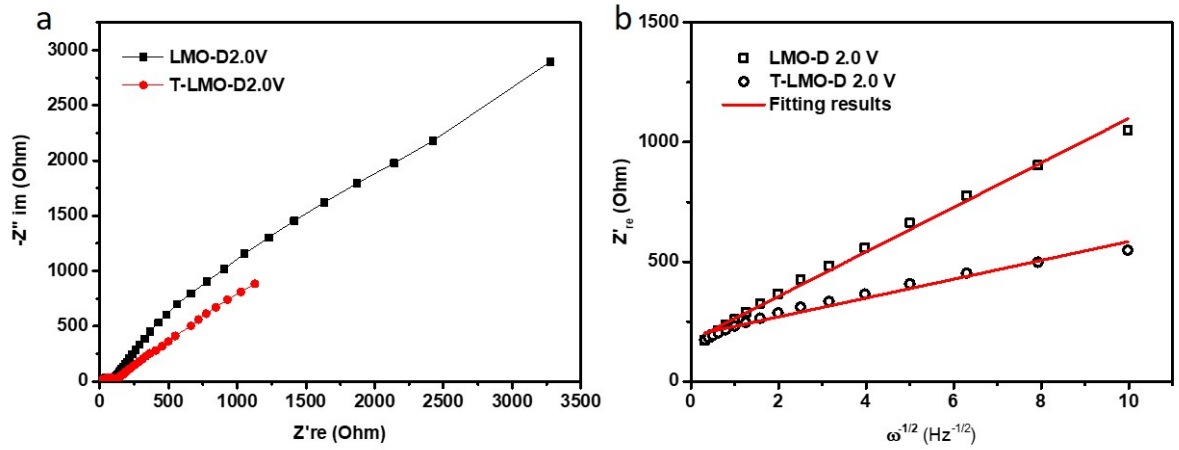


Supplementary Figure 1. (a) The average voltage evolution during cycling for pristine and treated LMO. The average voltage during discharge is obtained via dividing the total energy density by the total discharge capacity measured in the working voltage range between 2.0 V and 4.8 V. **(b)** The dQ/dV plots for LMO. **(c)** The dQ/dV plots for T-LMO. **(d)** The rate capacities for pristine and treated LMO.



Supplementary Figure 2. (a) Nyquist plots of cells with LMO and T-LMO electrodes after initially charged and discharged to 2.0 V. **(b)** The profiles of Z'_{Re} vs. $\omega^{-1/2}$ from 0.1 Hz to 0.01 Hz after initially charged and discharged to 2.0 V. The diffusion coefficient D_{Li+} has been proved being inversely proportional to the slop of the line in (b).[1,2]

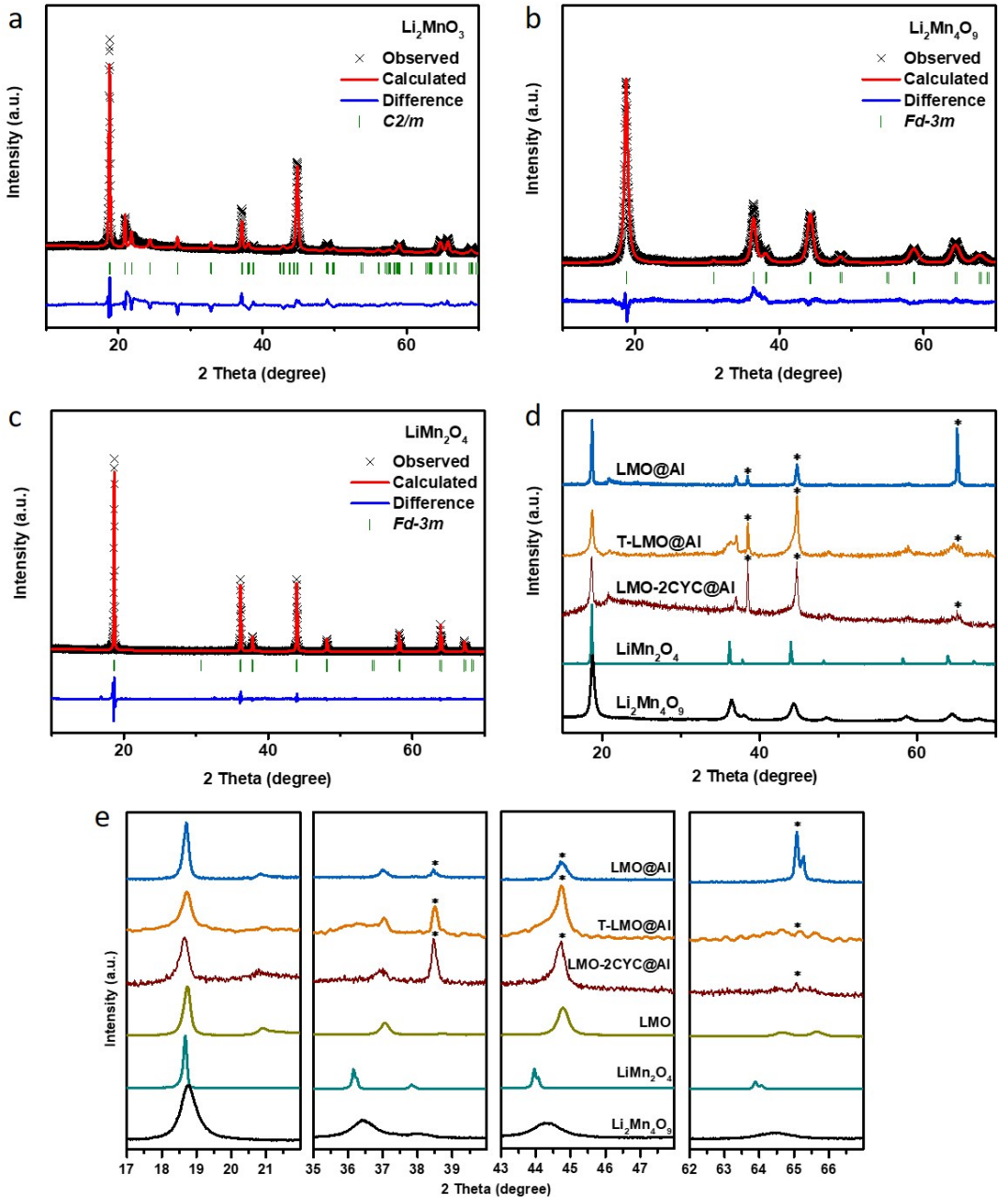
The Li^+ diffusion coefficient can be gained according to the following equation[1,2,3]:

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

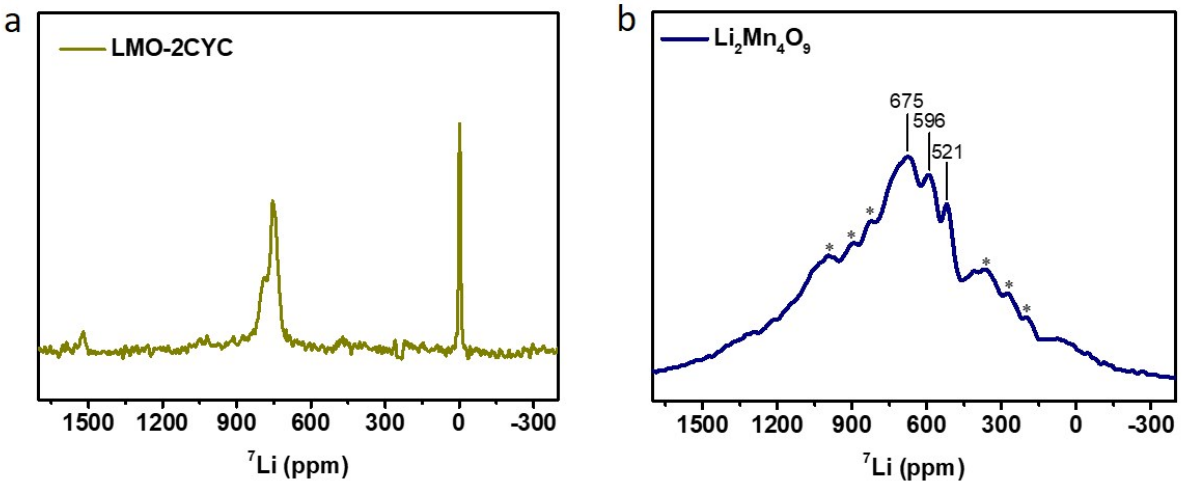
where D_{Li^+} represents the diffusion coefficient of Li ions, R is the gas constant, T is the absolute temperature, A is the surface area of electrode, n is the number of charges on the Li ion per molecule during oxidization, F is the Faraday constant, C is the concentration of Li ion, and σ the Warburg factor, σ relates to Z'_{Re} through the following equation:

$$Z'_{Re} = R_D + R_l + \sigma\omega^{-1/2}$$

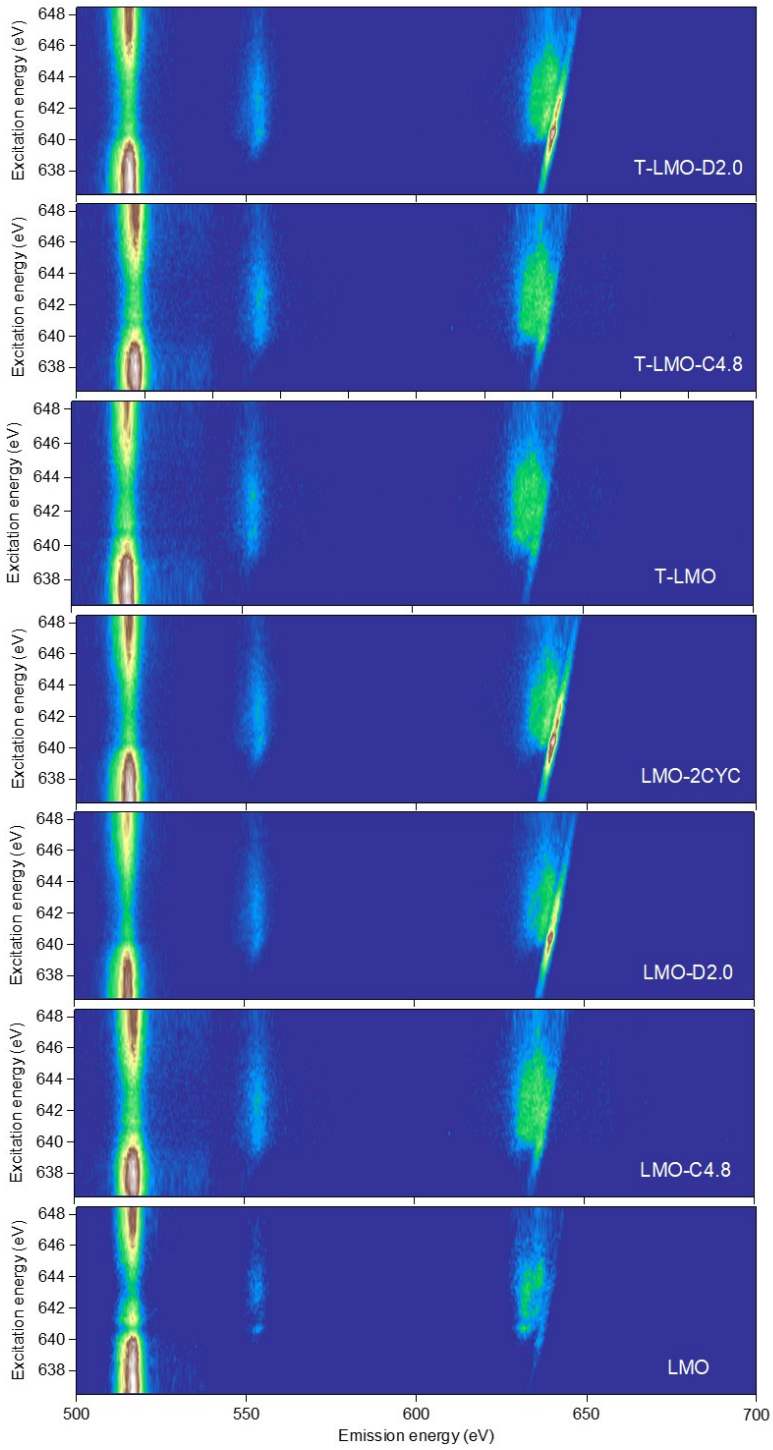
Therefore, the value of D_{Li^+} is inversely proportional to the Warburg factor, σ, that is the slop of the line in Figure S2b. From the results, T-LMO sample shows decreased slope of fitting line, indicating the enhanced Li^+ diffusion coefficient compared with that of pristine LMO. The slope of fitting line for T-LMO and LMO is 93.0 and 39.4. Therefore, the D_{Li+} for T-LMO is at least five times higher than that of LMO.



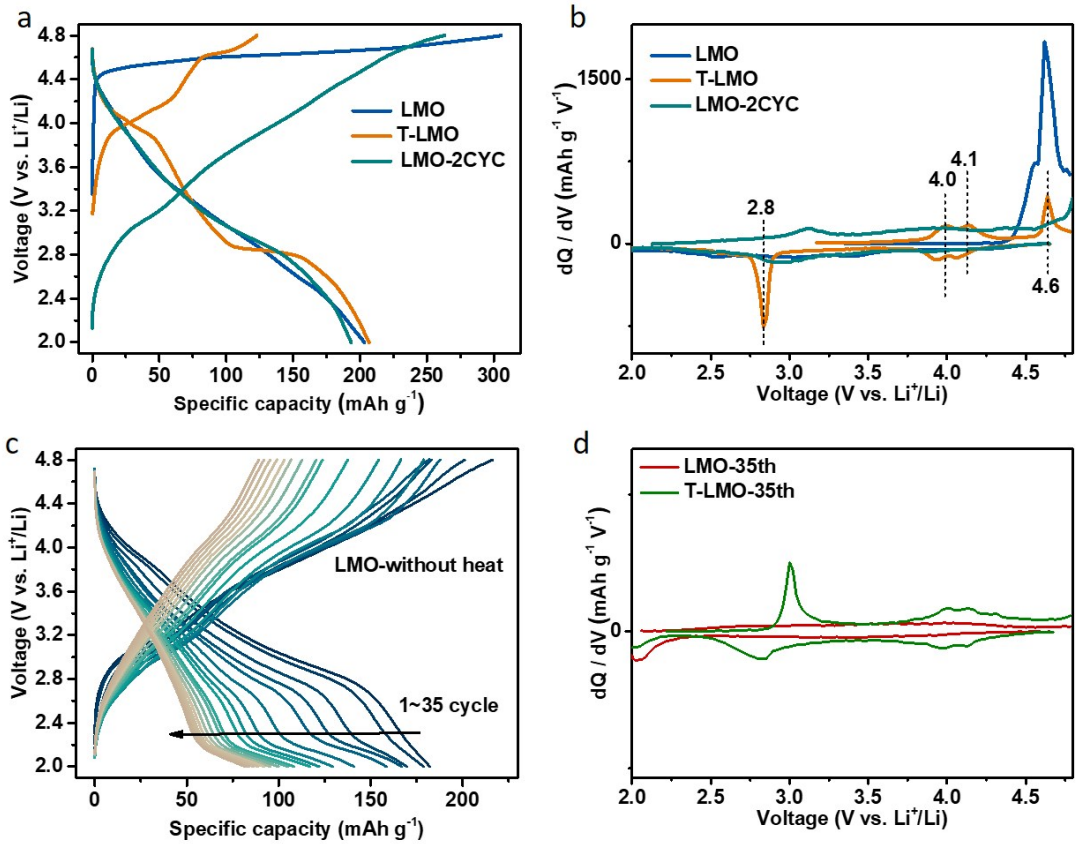
Supplementary Figure 3. The XRD patterns and Rietveld refinement for **(a)** pristine LMO **(b)** $Li_2Mn_4O_9$ and **(c)** $LiMn_2O_4$. The refinement parameters are in Table S1. **(d)** The comparison of XRD patterns and **(e)** enlarged profiles. The electrode samples in **(d)** and **(e)** were scraped from the electrode collector with residual aluminum powder, which is assigned as asterisk. For LMO, the peak at around 21° comes from Li/Mn order and stacking fault, which is excluded during refinement.[4] The defect spinel $Li_2Mn_4O_9$ can be described as $Li_{0.89}\square_{0.11}[Mn_{1.78}\square_{0.22}]O_4$.[5]



Supplementary Figure 4. (a) ^{7}Li pjMATPASS spectra for two cycled LMO material and **(b)** ^{7}Li NMR spectra for $Li_2Mn_4O_9$ material. The asterisk indicates spinning sidebands, which is consistent with previous result.[6]



Supplementary Figure 5. The original Mn-*L* mRIXS for LMO series samples.



Supplementary Figure 6. (a) The charge-discharge curves and **(b)** dQ/dV plots for pristine LMO in the initial cycle, second cycle and treated LMO in the initial cycle. **(c)**The cycling curves of LMO cycled twice and without thermal treatment. **(d)** dQ/dV plots for pristine LMO and T-LMO in the 35th cycle.

Supplementary Table 1. Refined crystallographic parameters of the XRD patterns.

LMO

Space group: *C2/m.*

Lattice parameters: a=4.9321(61) Å, b=8.5300(25) Å, c=5.0225(06) Å, α=90.000(0)°, β=109.138(9)°, γ=90.000(0)°.

Agreement factors: R_{wp}=10.0 %, R_p=6.5 %, χ^2=5.67.

Atom	x	y	z	Multiplicity	Occupancy	Uiso
Mn1	0.0000	0.1748	0.0000	4	1.0000	0.00500
Li1	0.0000	0.5000	0.0000	2	1.0000	0.00500
Li2	0.0000	0.0000	0.5000	2	1.0000	0.00500
Li3	0.0000	0.6617	0.5000	4	1.0000	0.00500
O1	0.2773	0.0000	0.1728	4	1.0000	0.00500
O2	0.2647	0.3313	0.2267	8	1.0000	0.00500

$Li_2Mn_4O_9$

Space group: *Fd-3m.*

Lattice parameters: a=8.1698(20) Å, b=8.1698(20) Å, c=8.1698(20) Å, α=90.000(0)°, β=90.000(0)°, γ=90.000(0)°.

Agreement factors: R_{wp}=14.5 %, R_p=12.4 %, χ^2=10.23.

Atom	x	y	z	Multiplicity	Occupancy	Uiso
Li1	0.1250	0.1250	0.1250	8	0.8800	0.00500
Mn1	0.5000	0.5000	0.5000	16	0.8817	0.00500
O2	0.2673	0.2673	0.2673	32	1.0000	0.00500

$LiMn_2O_4$

Space group: *Fd-3m.*

Lattice parameters: a=8.2415(26) Å, b=8.2415(26) Å, c=8.2415(26) Å, α=90.000(0)°, β=90.000(0)°, γ=90.000(0)°.

Agreement factors: R_{wp}=14.8 %, R_p=10.5 %, χ^2=8.299.

Atom	x	y	z	Multiplicity	Occupancy	Uiso
Li1	0.0000	0.5000	0.0000	2	1.0000	0.00500
Mn1	0.0000	0.1748	0.0000	4	1.0000	0.00500
O2	0.2647	0.3313	0.2267	8	1.0000	0.00500

Supplementary Table 2. The percentage distribution and average value of manganese valence by fitting the Mn-*L* iPFY spectra.

Sample	Mn^{2+} (%)	Mn^{3+} (%)	Mn^{4+} (%)	Average valence
LMO	0.0	0.0	100.0	4.00
LMO-C4.8	3.7	8.1	88.2	3.85
LMO-D2.0	15.0	53.1	31.9	3.17
LMO-2CYC	17.3	68.6	14.1	2.97
T-LMO	0.0	25.5	74.5	3.75
T-LMO-C4.8	0.5	9.0	90.5	3.90
T-LMO-D2.0	14.7	54.5	30.8	3.16

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